Table I. Absorption Maxima, Singlet State Energies, and Relative Rate Constants for Triplet Quenching by $O_2(^3\Sigma_g^-)$ of Trihexylsiloxymetal 2,3-Naphthalocyanines and Trihexylsiloxysilicon 2/3-Tetrahalo-2,3-naphthalocyanines in Various Solvents (25 °C)

no.	metal[a]	halogen	solvent[b]	λ_{max}[c] (nm)	E_S[d] (kcal/mol)	$k_{T\Sigma}^{Nc}/k_{T\Sigma}^{An}$[e]
1	Al		DMA	754	37.8	0.43
2	Ga		DMA[f]	765	37.3	0.11
3	Si		C_6H_{12}	767	37.2	0.20
4	Si	Cl	TMB	774	36.8	0.20
5	Si		C_6H_6	775	36.8	0.13
6	Si		TMB	776	36.8	0.14
7	Si	Br	TMB	776	36.8	0.20
8	Al		Py	776	36.7	0.069
9	Si		DMA	777	36.7	0.068
10	Sn		C_6H_{12}	778	36.7	0.041
11	Sn		C_6H_6	788	36.2	0.030
12	Ga		C_6D_6[f]	794	35.9	0.024
13	Ga		TMB	795	35.9	0.021
14	Al		TMB	796	35.8	0.017
15	Sn		TMB	797	35.8	0.019

[a] The Al and Ga naphthalocyanines carry one trihexylsiloxy group as an axial ligand, while the Si and Sn naphthalocyanines carry two *trans*-trihexylsiloxy groups. [b] Abbreviations: DMA = *N*,*N*-dimethylacetamide, C_6H_{12} = cyclohexane, TMB = 1,2,4-trimethylbenzene, Py = pyridine. [c] Q-band absorption maximum; ±0.5 nm. [d] ±0.1 kcal/mol. [e] ±10% except for no. 1 (±20%). [f] Solution contained 5–8 mM of either sodium azide (in DMA) or 1,4-diazabicyclo[2.2.2]octane (in TMB).

When the two triplet decay components were not clearly resolvable, a singlet oxygen quencher (either sodium azide or 1,4-diazabicyclo[2.2.2]octane) was added to make the decay exponential. Separate experiments in which both components of the triplet decay were resolvable verified that this quenching technique was valid. Further, the possibility[8] that electron transfer from the triplet to O_2 $(^3\Sigma_g^-)$ occurred in the most polar solvent employed, *N*,*N*-dimethylacetamide, was ruled out by the absence of residual transients following the decay of the triplet.[9]

The naphthalocyanines and solvent systems examined are listed in Table I.[13] The peak position of the lowest energy absorption band (λ_{max}) depended on solvent for all the naphthalocyanines, but the greatest range of band maxima was obtained with AlNcOSi(n-C_6H_{13})$_3$ (Table I, Figure 1 (inset)). The singlet energy (E_S) is usually taken to be midway between the energies of the 0,0 transitions in the absorption and fluorescence spectra: $E_S = (^1/_2)(E_{max}^{abs} + E_{max}^{fl})$. The fluorescence spectra of the naphthalocyanines mirrored the absorption, and the Stokes shifts between the 0,0 band maxima were in the range 2–6 nm (0.1–0.3 kcal/mol). For simplicity, an average Stokes shift of 0.2 kcal/mol was assumed for all solutions. The values of E_S were thus obtained by subtracting 0.1 kcal/mol from E_{max}^{abs}. Figure 1 shows the plot of the data in the last column of Table I vs E_S. The theoretical curve in this plot was obtained from eq 4 with E_{ST} = 15.6 kcal/mol. The data points fall within the limits determined by E_{ST} = 15.6 ± 0.4 kcal/mol, which is in agreement with the value determined spectroscopically for SiNc (E_{ST} = 15.4 kcal/mol).[1] We conclude that the fact that the Sandros equation relates the T_1 quenching constants of the naphthalocyanines to their S_1 energies arises because the S_1–T_1 energy gap is determined primarily by the ring skeleton and is not significantly influenced by the central metals or solvents examined.

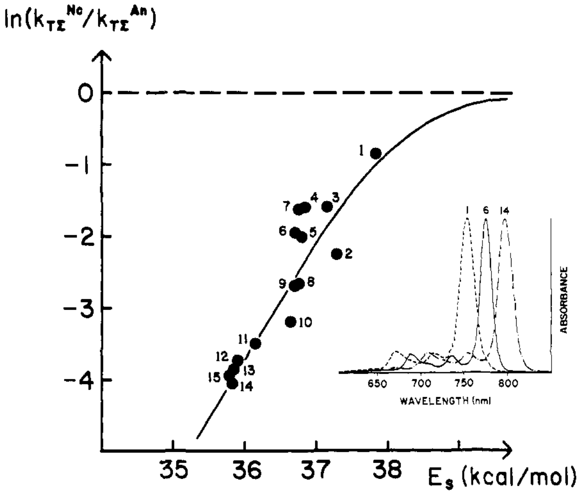

Figure 1. Dependence of rate constant for Nc triplet quenching by O_2 on the naphthalocyanine singlet excited state energy. The rate constants for the naphthalocyanines are relative values compared to the rate constant for quenching of the triplet of 2′-acetonaphthone in the same solvent. The experimental points are numbered according to the sequence in Table I. The theoretical line is calculated according to eq 4 with E_{ST} = 15.6 kcal/mol (E_Δ = 22.5 kcal/mol). Inset: representative absorption spectra of AlNcOSi(n-C_6H_{13})$_3$ in DMA (no. 1), SiNc(OSi(n-C_6H_{13})$_3$)$_2$ in TMB (no. 6), and AlNcOSi(n-C_6H_{13})$_3$ in TMB (no. 14) normalized to the same relative maximal absorbance.

Acknowledgment. Support for this project came in part from NIH Grant 24235 and the Center for Photochemical Sciences at Bowling Green State University. We are grateful to Dr. A. A. Gorman for valuable commentary and to Drs. L. A. Schechtman and J. R. Sounik for the preparation of some of the compounds employed.

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(5) Murov, S. *Handbook of Photochemistry*; Dekker: New York, 1973; p 89.

(6) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 311–316.

(7) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1–90.

(8) We acknowledge a referee for raising this question.

(9) No long-lived (>5 μs) transients absorbing in the wavelength range 450–670 nm were observed in an O_2-saturated solution of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ in *N*,*N*-dimethylacetamide containing NaN_3 (8 mM) following the decay of the triplet state. On the basis of the approximate reduction potentials (vs NHE) of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ ($SiNc^{\bullet+}/SiNc$, $E° \approx +0.8$ V)[10] and azide ion ($N_3^\bullet/N_3^-$, $E° \approx +1.3$ V),[11] azide ion should not reduce the naphthalocyanine radical cation, which would be produced if electron transfer to O_2 $(^3\Sigma_g^-)$ occurred. Thus, we conclude that electron transfer can be neglected as a triplet quenching mechanism. Moreover, the triplet state of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ is estimated to have a reduction potential $E° \approx -0.1$ V, which is 0.5 V more positive than the potential required to reduce O_2 to $O_2^{\bullet-}$ in this solvent.[12]

(10) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404–7410.

(11) (a) Ram, M. S.; Stanbury, D. M. *J. Phys. Chem.* **1986**, *90*, 3691–3696. (b) Alfassi, Z. B.; Harriman, A.; Huie, R. E.; Mosseri, S.; Neta, P. *J. Phys. Chem.* **1987**, *91*, 2120–2122.

(12) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393–400.

(13) A synthesis of SiNc(OSi(n-C_6H_{13})$_3$)$_2$ has been given earlier.[10] Syntheses of the remaining compounds will be given in subsequent papers.

A Stereoselective Synthesis of Functionalized Alkenyllithiums and Alkenyl Cyanocuprates by the Cu(I)-Catalyzed Coupling of Organolithium Reagents with α-Lithiated Cyclic Enol Ethers

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The α-metalation of cyclic enol ethers with organolithium reagents is a clean and efficient process which has been extensively exploited in synthesis.[1,2] Far less familiar are the reactions of

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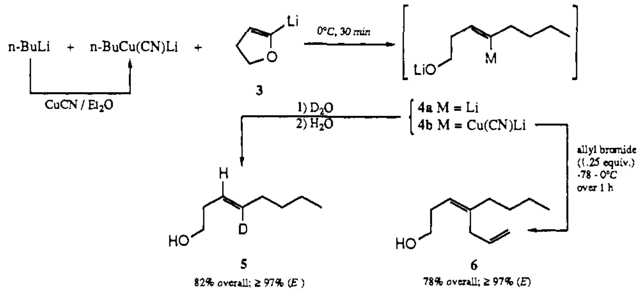
Scheme I



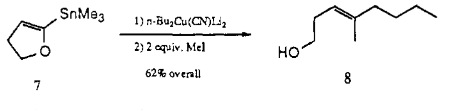
cyclic enol ethers with organolithium and Grignard reagents which result in ring cleavage via an apparent nucleophilic displacement. For example, 3,4-dihydro-2H-pyran (**1**) reacts with primary alkyl and aryl Grignard reagents to give alkenols **2** in modest yield (eq 1).[3] A similar reaction occurs on treatment of **1** with alkyllithiums

(1)

at elevated temperature.[4] The efficiency of these reactions is greatly enhanced by the addition of transition metals such as Cu(I)[5] and Ni(0).[6] With the exception of the Ni(0)-catalyzed coupling of Grignard reagents with dihydropyrans and dihydrofurans,[7] few of these reactions have been turned to advantage in synthesis.

We now report a new connective and stereoselective synthesis of functionalized alkenyllithiums (Scheme I) or the corresponding alkenyl cyanocuprates which is based on the CuCN-catalyzed union of an α-lithiated cyclic enol ether with an organolithium reagent. The reaction of 5-lithio-2,3-dihydrofuran (**3**) with n-BuLi illustrates the procedure. To a stirred suspension of CuCN (0.3 mmol, 0.1 equiv) in Et$_2$O was added at 0 °C n-BuLi in hexane (4.0 mmol). The resultant mixture was stirred for 30 min and cooled to −20 °C whereupon a solution of **3** (3.0 mmol) in Et$_2$O was added, and the mixture was stirred at −20 °C for 30 min. After quenching with excess D$_2$O and standard aqueous workup, the product was purified by column chromatography on silica gel (Et$_2$O/hexane = 1:4) and Kugelrohr distillation to give (E)-4-deuteriooct-3-en-1-ol (**5**) in 82% yield. The intermediate in this reaction was presumably a mixture of the alkenyllithium **4a** and the cyanocuprate **4b**.

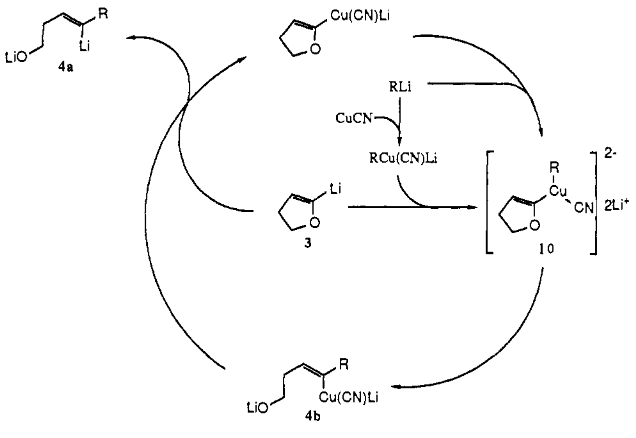
A similar procedure can be used to generate the cyanocuprate[8] intermediate **4b** exclusively. Thus repetition of the reaction with 3 mmol (1 equiv) of CuCN gave **4b** which reacted with allyl bromide at −78 °C to give the trisubstituted alkene **6** in 78% yield. Alternatively, 5-(trimethylstannyl)-2,3-dihydrofuran (**7**) can be added to a solution of the higher order cyanocuprate n-Bu$_2$Cu(CN)Li$_2$ to give **4b** which then furnished the trisubstituted alkene **8** on reaction with MeI.[9]



(2)

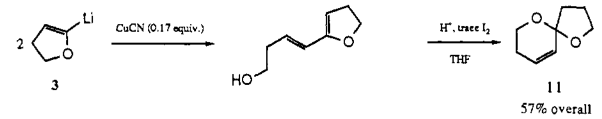
The Cu(I)-catalyzed coupling of a variety of organolithium reagents with **3** and the homologous 6-lithio-3,4-dihydro-2H-pyran (**9**)[10] was examined with the general procedure outlined above, and the efficiency of the coupling was assayed by isolation of the deuterated or protonated alkenol product as shown in Scheme I. As can be seen from the results summarized in Table I, the reaction has remarkably broad scope: MeLi, primary, secondary, and tertiary alkyllithiums, PhLi, CH$_2$=C(Me)Li, Me$_3$SnLi, and PhMe$_2$SiLi participate in the reaction. With the exception of MeLi, PhLi, and alkynyllithiums, the yield of the coupling products is generally good. As little as 2 mol% of CuCN is required to catalyze the reaction when organolithium reagents are reaction partners; with Grignard reagents, however, 1 equiv of CuCN must be used to get good yields (entry 8).

Scheme II



One possible mechanism which accounts for the catalytic nature of the coupling reaction is shown in Scheme II. According to this hypothesis, the key steps in the transformation are (1) the formation of the higher order cyanocuprate intermediate **10** and its rearrangement[11] with inversion of configuration at the alkenylmetal center and (2) the subsequent transmetalation of **4b** to **4a** in which the alkenyl ligand is displaced by the dihydrofuranyl ligand. According to this mechanism, the inefficiency of the reactions of MeLi (entry 4), PhLi (entry 6), and alkynyllithiums reflects the low migratory aptitudes of methyl, phenyl, and alkynyl ligands leading to competing self-coupling of the enol ether ligands (vide infra).

Scheme III



Scheme III illustrates the effect of using a homo- rather than mixed organocuprate (i.e., **10**, R = dihydrofuranyl) for this

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(1) Riobe, O.; Lebouc, A.; Delaunay, J. *C.R. Acad Sci. Paris Ser C* **1977**, *284*, 281. Ruzziconi, R.; Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 855. Kocieński, P.; Yeates, C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1879. Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E. *J. Chem. Soc., Chem. Commun.* **1986**, 925. Hanessian, S.; Martin, M.; Desai, R. C. *J. Chem. Soc., Chem. Commun.* **1986**, 926. Lesimple, P.; Beau, J.-M.; Jaurand, G.; Sinaÿ, P. *Tetrahedron Lett.* **1986**, *27*, 6201. Smith, A. B.; Fukui, M. *J. Am. Chem. Soc.* **1987**, *109*, 1269. Boeckman, R. K.; Charette, A. B.; Asberom, T.; Johnston, B. H. *J. Am. Chem. Soc.* **1987**, *109*, 7553. Whitby, R.; Kocieński, P. *J. Chem. Soc., Chem. Commun.* **1987**, 906. Funk, R. L.; Bolton, G. L. *Tetrahedron Lett.* **1988**, *29*, 1111.

(2) In certain instances β-metalation of enol ethers can be observed: Paul, R.; Tchelitcheff, S. *C.R. Acad. Sci. Paris* **1952**, *235*, 1226. Ficini, J.; Kahn, P.; Falou, S.; Touzin, A. M. *Tetrahedron Lett.* **1979**, 67. McDougal, P. G.; Rico, J. G.; Van Derveer D. *J. Org. Chem.* **1986**, *51*, 4492.

(3) Hill, C. M.; Senter, G. W.; Haynes, L.; Hill, M. E. *J. Am. Chem. Soc.* **1954**, *76*, 4538.

(4) Pattison, F. L. M.; Dear, R. E. A. *Can. J. Chem.* **1963**, *41*, 2600. Stähle, M.; Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1977**, *60*, 1730.

(5) Fujisawa, T.; Kurita, Y.; Kawashima, M.; Sato, T. *Chem. Lett.* **1982**, 1641.

(6) Wenkert, E.; Michelotti, E. L.; Swindell, C. S.; Tingoli, M. *J. Org. Chem.* **1984**, *49*, 4894.

(7) Wadman, S.; Whitby, R.; Yeates, C.; Kocieński, P.; Cooper, K. *J. Chem. Soc., Chem. Commun.* **1987**, 241. Kocieński, P.; Dixon, N. J.; Wadman, S. *Tetrahedron Lett.* **1988**, *29*, 2353; Kocieński, P.; Wadman, S.; Cooper, K. *Tetrahedron Lett.* **1988**, *29*, 2357. Kocieński, P.; Love, C.; Whitby, R.; Roberts, D. A. *Tetrahedron Lett.* **1988**, *29*, 2867.

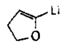
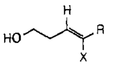
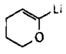
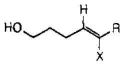
(8) Review: Lipshutz, B. H. *Synthesis* **1987**, 325.

(9) For the transmetalation between alkenylstannanes and higher order cyanocuprates, see: Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641.

(10) Boeckman, R. K.; Bruza, K. J. *Tetrahedron* **1981**, *37*, 3997.

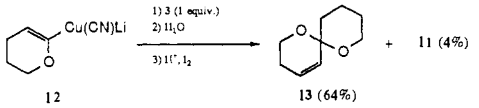
(11) An analogous 1,2-alkyl shift involving enol ether boronates is known: Levy, A. B.; Schwartz, S. J. *Tetrahedron Lett.* **1976**, 2201.

Table I. Cu(I)-Catalyzed Reaction of Organolithium Reagents with **3** and **9**

entry	α-lithio enol ether	organolithium	equiv CuCN	quench	product (% yield)[d-f]
					
1	**3**[a]	*n*-BuLi	0.1	D_2O	X = D, R = *n*-Bu (82%)
2		*s*-BuLi	0.1	H_2O	X = H, R = *s*-Bu (88%)
3		*t*-BuLi	0.1	D_2O	X = D, R = *t*-Bu (77%)
					
4	**9**	MeLi	0.1	H_2O	X = H, R = Me (52%)
5		*n*-BuLi	1.0	D_2O	X = D, R = *n*-Bu (78%)
6		PhLi	1.0	D_2O	X = D, R = Ph (25%)
7		$CH_2{=}C(Me)Li$	0.07	H_2O	X = H, R = $CH_2{=}C(Me)$ (79%)
8		$PhCH_2MgBr$	1.0	D_2O	X = D, R = $PhCH_2$ (60%)
9		$PhMe_2SiLi$[b]	0.2	H_2O	X = H, R = $PhMe_2Si$ (92%)
10		Me_3SnLi[c]	0.2	H_2O	X = H, R = Me_3Sn (78%)[g]

[a] Reaction performed in one pot by adding 2,3-dihydrofuran to a mixture prepared from the alkyllithium (2.4 equiv) and CuCN. [b] Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527. [c] Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237. [d] Yields refer to products purified by column chromatography and Kugelrohr distillation. [e] All products were characterized by ^1H NMR (270 MHz), ^{13}C NMR (67.5 MHz), IR, and high resolution EIMS. [f] Isomeric purity (≥97%) was ascertained by NMR spectroscopy and capillary GC. [g] Yield refers to product purified by column chromatography only.

coupling. In this case the lithiated enol ether **3** reacted with itself[12] to give a coupling product which cyclized to 1,7-dioxaspiro[5.4]dec-4-ene (**11**) on treatment with a trace of *p*-toluenesulfonic acid in the presence of I_2.[13] This procedure can also be used to achieve a cross-coupling of enol ethers. Thus, treatment of the cyanocuprate **12**[14] with lithiated dihydrofuran **3** gave an intermediate which underwent chemoselective cleavage of the more reactive dihydrofuran ring affording 1,7-dioxaspiro[5.5]undec-4-ene (**13**) preferentially.



12 13 (64%) (3)

In conclusion, the Cu(I)-catalyzed coupling of α-lithiated cyclic enol ethers with organolithium reagents has several commendable virtues: it is connective, stereoselective, easy to do, generally efficient, and broad in scope. It provides a welcome addition to the meager repertoire of synthetic routes to the versatile alkenyllithiums.[15] The value of the method is presaged in this work by stereoselective syntheses of alkenylsilanes, alkenylstannanes, trisubstituted alkenes, and unsaturated spiroacetals.

Acknowledgment. We thank the Science and Engineering Research Council of Great Britain for a CASE Studentship and Christopher Barber for some additional experiments.

Supplementary Material Available: Experimental and spectral data (IR, ^1H NMR, and ^{13}C NMR) for **6**, **8**, **11**, **13**, and other compounds (5 pages). Ordering information is given on any current masthead page.

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(12) 6-Lithio-3,4-dihydro-2*H*-pyran (**9**) also couples with itself in the absence of other organolithium reagents but attempts to spirocyclize the product have failed to return a stable spiroacetal.

(13) Whitby, R.; Kocieński, P. *Tetrahedron Lett.* **1987**, *28*, 3619.

(14) Organocuprate derivatives of enol ethers have been prepared previously: Kocieński, P.; Yeates, C. *Tetrahedron Lett.* **1983**, *24*, 3905; Kocieński, P.; Street, S. D. A.; Yeates, C.; Campbell, S. F. *J. Chem. Soc. Perkin Trans. 1* **1987**, 2189. Boeckman, R. K.; Bruza, K. J.; Baldwin, J. E.; Lever, O. W. *J. Chem. Soc., Chem. Commun.* **1975**, 519. Chavdarian, C. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 3822.

(15) Wardell, J. L. *Comp. Organometallic Chem.* **1982**, *1*, 91.

Book Reviews*

The Chemistry of Inorganic Homo- and Heterocycles. Volumes 1 and 2. Edited by Ionel Haiduc and D. B. Sowerby (Babes-Bolyai University, Cluj-Napoca, Romania, and University of Nottingham). Academic Press: Orlando, 1987. Volume 1: xxiv + 416 + XI pp. $108.00. ISBN 0-12-655775-6. Volume 2: xxiv + 471 + XI pp. $117.00. ISBN 0-12-655776-4. $196.50 the set.

The chemistry of inorganic ring systems was admirably reviewed in an earlier monograph by Haiduc (Haiduc, Ionel, "The Chemistry of Inorganic Ring Systems", Wiley-Interscience: New York, 1970), and he has restarted his reviewing of the topic in 1979, as a series of annual events. A 10-year gap in comprehensive reviews of the topic exists, however. It is the purpose of the present volumes to fill that gap, and the job has been as well done as Haiduc has led us to expect from him.

The "Introduction" in Volume 1 defines inorganic rings for us ("an inorganic ring is a finite polynuclear system of atoms other than carbon, arranged to form a closed (planar or close to planar) structure, made up of identical atoms (homocycle) or different atoms (heterocycle)"—the definition is applied only to main-group elements in these volumes) and gives an account of the different nomenclature systems used to describe these rings. What a collection of reviews then follows for almost 900 pages! A total of 25 authors, all experts in their own areas, give us chapters on B homocycles (2 pp, 8 ref); B–N heterocycles (73 pp, 414 ref); B–P and B–As heterocycles (6 pp, 22 ref); B–O heterocycles (22 pp, 420 ref); B–S and B–Se heterocycles (21 pp, 78 ref); Al–N rings and cages (21 pp, 113 ref); Si homocycles (26 pp, 183 ref); Si–N heterocycles (49 pp, 237 ref); Si–P heterocycles (9 pp, 35 ref); Si–O heterocycles (33 pp, 936 ref); Si–S heterocycles (9 pp, 56 ref); Ge homocycles (4 pp, 20 ref); Ge heterocycles (8 pp, 76 ref); cyclostannanes (4 pp, 10 ref); Sn–N and Sn–P heterocycles (17 pp, 46 ref); Sn–O, Sn–S, Sn–Se, and Sn–Te heterocycles (15 pp, 59 ref); N homocycles (4 pp, 46 ref); P homocycles (38 pp, 207 ref); P(III)–N heterocycles (29 pp, 164 ref); cyclophosphazenes (87 pp, 1057 ref); cyclophosph(V)azanes (37 pp, 149 ref); P–O heterocycles (18 pp, 129 ref); P–S and P–Se rings and cages (17 pp, 115 ref); As homocycles (9 pp, 59 ref); As–N, As–O, As–S, and As–Se heterocycles (15 pp, 75 ref); Sb and Bi homocycles and heterocycles (6 pp, 41 ref); S homocycles (26 pp, 160 ref); Se homocycles and S–Se heterocycles (21 pp, 101 ref); S–N heterocycles (65 pp, 476 ref); and S–O, Se–O, and Se–N heterocycles (6 pp, 34 ref).

The references in these articles are about 90% from the 1969–80 time span, with 1% from before that period and the remainder from 1980 on. The chapters are highly individual in their presentation of material and

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